Surfactant-Directed Polypyrrole/CNT Nanocables: Synthesis, Characterization, and Enhanced Electrical Properties

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We describe here a new approach to the synthesis of size-controllable polypyrrole/carbon nanotube (CNT) nanocables by in situ chemical oxidative polymerization directed by the cationic surfactant cetyltrimethylammonium bromide (CTAB) or the nonionic surfactant polyethylene glycol mono-p-nonylphenyl ether (Oπ–10). When carbon nanotubes are dispersed in a solution containing a certain concentration of CTAB or Oπ–10, the surfactant molecules are adsorbed and arranged regularly on the CNT surfaces. On addition of pyrrole, some of the monomer is adsorbed at the surface of CNTs and/or wedged between the arranged CTAB or Oπ–10 molecules. When ammonium persulfate (APS) is added, pyrrole is polymerized in situ at the surfaces of the CNTs (core layer) and ultimately forms the outer shell of the nanocables. Such polypyrrole/CNT nanocables show enhanced electrical properties; a negative temperature coefficient of resistance at 77–300 K and a negative magnetoresistance at 10–200 K were observed.

Introduction

The past decade has witnessed significant progress in both the production and application of carbon nanotubes (CNTs) since their discovery in 1991.[1–2] Following the first report of the preparation of a CNT/polymer composite by Ajayan et al.,[3] many efforts have been made to combine CNTs and polymers to produce functional composite materials with superior properties.[4–7] For example, epoxy resin loaded with 1% carbon single-walled nanotubes (SWNTs) showed a increase in thermal conductivity of 70% at 40 K and 125% at room temperature.[8] The presence of SWNTs in poly(m-phenylene vinylene-co-2,5-dioctoxy-p-phenylene) (PmPV) composites shifts the radiative recombination region in double-emitting organic light-emitting diodes (DE-OLEDs) without changing the emission energy of PmPV.[9] Addition of only 1% carbon multiwalled nanotubed (MWNTs) to polystyrene results in a significant increase in the mechnical properties of the polymer because the external load can be effectively transferred to the nanotubes,[10] and the introduction of MWNTs into polyaniline composites enhances the electrical properties by facilitating charge-transfer processes between the two components.[11]

Recently, several methods to produce CNT/polymer composites have been developed, including dissolving polymers in a suspension of CNTs in organic solvents, melt mixing, in situ polymerization, wrapping nanotubes with polymer chains, grafting macromolecules onto CNTs, and electrochemistry.[12–16] Despite these efforts, the study of CNT composite materials has been hindered by the poor solubility and processibility of CNTs. Researchers have addressed these problems by using surfactants or modifying the surfaces of nanotubes. Here we describe a simple approach to the synthesis of size-controllable polypyrrole/CNT nanocables by in situ chemical oxidative polymerization directed by different types of surfactants. Such polypyrrole/CNT nanocables show enhanced electrical properties due to their cablelike structure.

Results and Discussion

The morphologies of nanostructures prepared with cationic and nonionic surfactants were characterized by SEM and TEM (Figure 1). The TEM images (Figure 1b and d) revealed that whatever surfactant was used, the as-prepared nanostructures exhibited hollow cores. The SEM images also showed that for both surfactants used the nanostructures obtained were of roughly uniform size with diameters in the range of several tens of nanometers and lengths of up to several micrometers. The length of the nanostructures was strongly related to the length of the CNTs. Nanostructures directed by the cationic surfactant cetyltrimethylammonium bromide (CTAB) were relatively smooth (Figure 1a), but the surfaces of those prepared with the nonionic surfactant Oπ–10 bore spherical particles (Figure 1c) with diameters of about half of that of nanostructures themselves. High-resolution TEM (HRTEM; Figure 1e) clearly revealed a cablelike structure in which the outer layer was apparently amorphous (arrow, Figure 1e) and the inner

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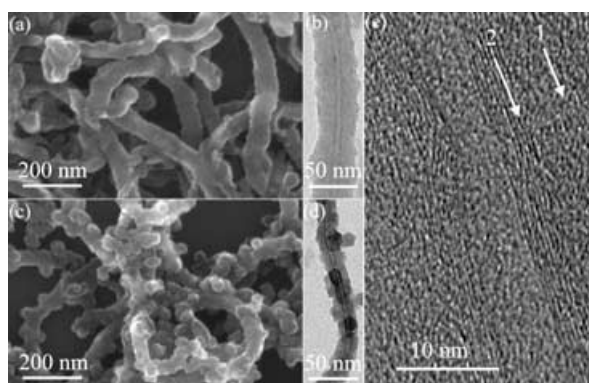Peking University, Beijing 100871 (P.R. China)

Figure 1. *Surfactant-directed polypyrrole/CNT nanocables: SEM image of CTAB-directed nanocables (a), TEM image of an individual CTAB-directed nanocable (b), SEM image of Oπ–10-directed nanocables (c); TEM image of an individual Oπ–10-directed nanocable (d), and HRTEM image of an individual CTAB-directed nanocable (e).*

layer was crystalline (arrow 2, Figure 1e). A lattice spacing of about 0.34 nm along the nanocables could be readily resolved and indicates that the inner layer consists of multiwalled CNTs.[19] Taken together, these data suggest that the pyrrole monomers polymerize not in the hollow core but at the surface of the CNTs. The outer amorphous polypyrrole layer had an average thickness in the range of tens of nanometers.

The average diameter of the nanocables could be controlled by changing the pyrrole/CNT mass ratio. Typical CNTs without polypyrrole coatings were uniform with diameters in the range of 8–25 nm and lengths of up to several micrometers (Figure 2d), the distribution of diameters (obtained by measurement of hundreds of SEM images) at different locations showed a peak centered at 16 nm. Nanocables with different pyrrole/CNT mass ratios differed from CNTs in both structure and size (Figure 2a–c). The smaller the pyrrole/CNT mass ratio, the smaller the average diameter. This trend can be clearly seen from the histograms of diameter distributions. At pyrrole/CNT ratios below 10/3, many nanostructures with diameters corre-

sponding to that of the CNTs were seen. At a 10/3 pyrrole/CNT mass ratio, although diameters as small as those of pure CNTs were still present, a new peak appeared at a diameter of 29 nm. Increasing the pyrrole/CNT ratios to 20/3 and 30/3 resulted in mean diameters of 38 and 50 nm respectively. However, increasing the pyrrole/CNT ratio to greater than 30/3 gave no further increase in average diameter. In fact, at these ratios, TEM images revealed some pure polypyrrole nanowires. These data indicate that the optimum pyrrole/CNT mass ratio range lies between 10/3 and 30/3, and we can control the average diameter by simply changing the ratio in this range.

Figure 3a shows the IR spectrum of CTAB-directed polypyrrole/CNT nanocables. The polypyrrole/CNT nanocables directed by CTAB and by Oπ-10 showed nearly identical numbers and positions of the main IR bands. The broad band at 3000–3500 cm^{-1} could be attributed to N—H and C—H stretching vibrations,[20, 21] the strong peaks near 1195 and 920 cm^{-1} indicate the doping state of polypyrrole,[20, 21] and the peaks at 1050 cm^{-1} and 1315 cm^{-1} are attributed to C—H deformation
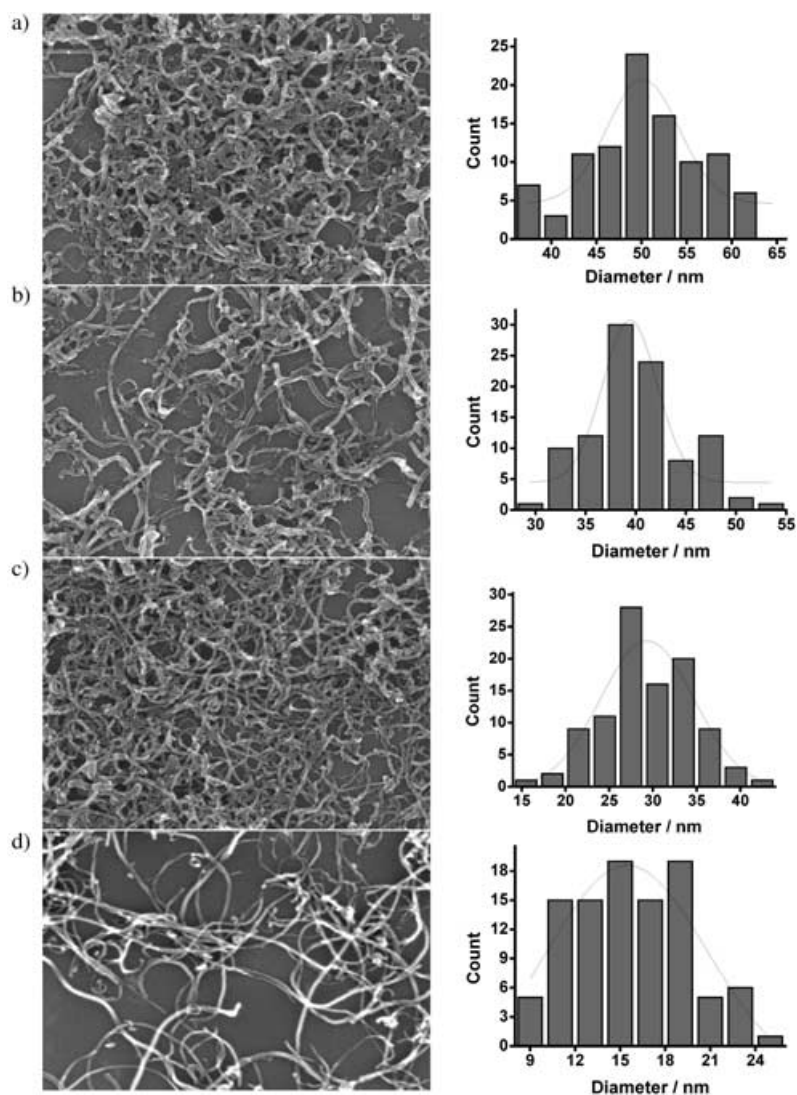

Figure 2. *SEM images and diameter distributions of polypyrrole/CNT nanocables with different pyrrole/CNT mass ratios: a) 30/3; b) 20/3; c) 10/3, d) 0/3.*
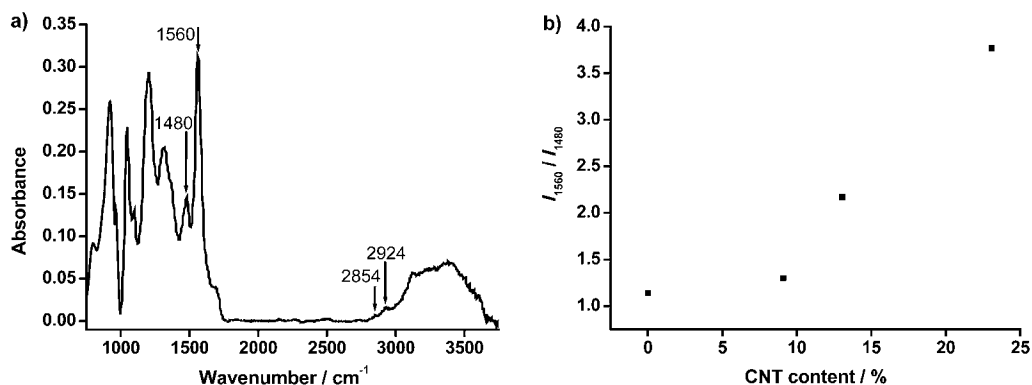
Figure 3. a) IR spectrum of CTAB-directed polypyrrole/CNT nanocable showing the 1560 cm^{-1} and 1480 cm^{-1} bands; b) plot of I$_{1560}$/I$_{1480}$ of nanocables with different pyrrole/CNT mass ratios.

and C–N stretching vibrations,[20, 21] respectively. In addition, the peaks around 1560 and 1480 cm^{-1} correspond to the asymmetric and symmetric ring-stretching modes, respectively.[22] The two very weak peaks around 2924 cm^{-1} and 2854 cm^{-1}, attributable to stretching modes of methyl and methylene groups, indicate that the surfactants were almost completely eliminated from the nanocables.

According to an analysis by Tian and Zerbi, the ratio of the integrated absorption intensities of the 1560 and 1480 cm^{-1} bands I$_{1560}$/I$_{1480}$ is inversely proportional to the extent of delocalization.[20, 21] Thus, polymers with high concentrations of defect sites (short conjugation lengths) showed high values of I$_{1560}$/I$_{1480}$, whereas polymers with low concentrations of defect sites (long conjugation lengths) showed low values of I$_{1560}$/I$_{1480}$. The calculated I$_{1560}$/I$_{1480}$ values of nanocables with different CNT contents are plotted in Figure 3 b. Note that I$_{1560}$/I$_{1480}$ increases with increasing CNT content of the nanocables (i.e., with decreasing thickness of the polypyrrole layer). This clearly shows that the layer of polypyrrole that is deposited directly on the surfaces of CNTs has a shorter conjugation length than subsequently deposited layers, probably due to the π–π interaction between CNTs and pyrrole monomers.

A possible mechanism of polypyrrole/CNT nanocable formation by in situ chemical oxidative synthesis in the presence of surfactants is shown in Figure 4. Initially, the surfactant separates the CNT bundles into individual tubes during sonication in water. Surfactant molecules are then adsorbed in a regular
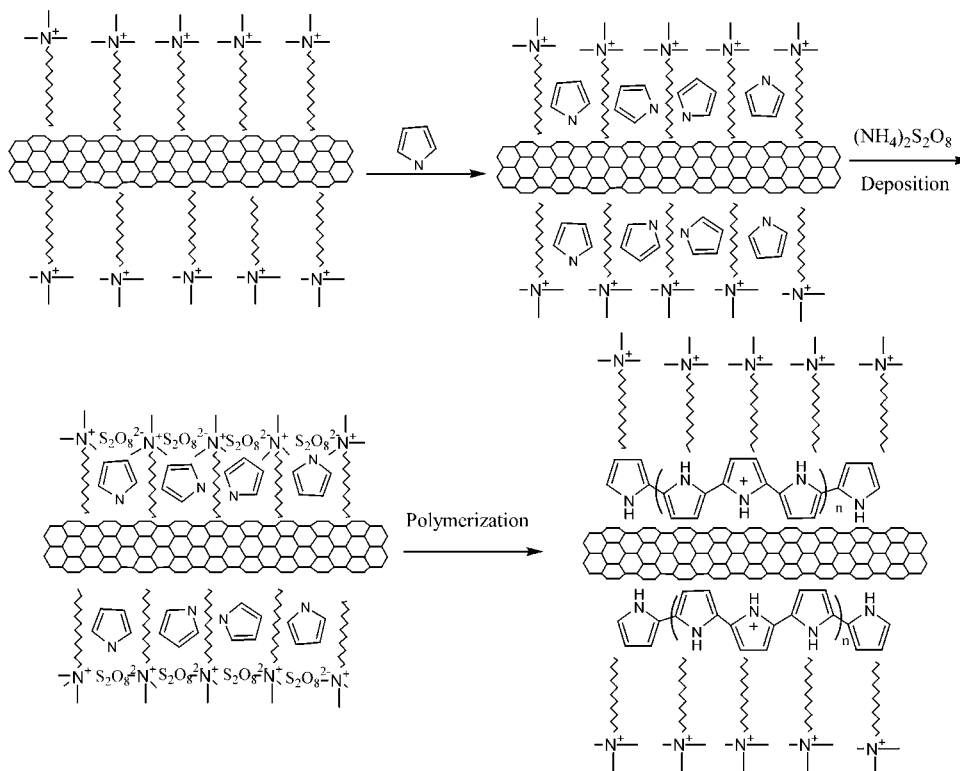

Figure 4. Schematic diagram of the mechanism of formation of polpyrrole/CNT nanocables.

pattern on the CNT surfaces.[18] A columnar microregion containing a hard core (CNT) and a soft interface (surfactant) is thus formed. On addition of the pyrrole monomers, due to their slight solubility in water and π–π interaction between monomers and CNTs, they insert themselves between the surfactant layer and the CNT. When APS was added to initiate polymerization, a heavy floccular precipitate appeared instantly, presumably due to electrical neutralization of the quaternary ammonium cation of CTAB by the S$_2$O$_8^{2-}$ ion of APS. Since (CTA)$_2$S$_2$O$_8$ is insoluble in water, the surfactant CTAB would therefore be deactivated, and both pyrrole and individual CNTs become entrapped in the precipitate. When a redox reaction between pyrrole and S$_2$O$_8^{2-}$ occurs, owing to the solubility of (CTA)$_2$SO$_4$ in water, the floccular precipitate gradually disap-

pears, and the surfactant CTAB is regenerated. At the same time, polypyrrole is gradually deposited on the surface of the CNTs. The resulting polypyrrole/CNT nanocable suspensions would then be stabilized by the regenerated surfactant. When the nonionic surfactant Oπ-10 is used, apart from the surfactant deactivation/regeneration step, the process would be similar to that directed by CTAB.

Anionic detergents such as sodium dodecyl sulfate did not produce such nanocables, probably because doped polypyrroles contain counterions in the polymer chains. Anionic surfactants would thus serve as counterions for the polymer chains and would thus permanently disrupt the structure of the columnar microregions, that is, no regeneration of surfactant would occur.

When the concentration of surfactants was between the two- and twelvefold critical micelle concentration (CMC), there was no clear difference in the diameters or morphologies of nanocables. When the concentration of surfactants was below twice the CMC, it was difficult to disperse CNTs into individual tubes and to maintain sufficiently stable CNT suspensions for formation of nanocables.

The pH also played a key role in the formation of polypyrrole/CNT nanocables. At pH ≈ 7, nanocables were formed with relatively smooth surfaces. In the pH range 0–7, surface irregularities appeared at the edges of the nanocables in the form of "dents" or depressions. These features increased in size with decreasing pH. Below pH 0, nanocables were not formed. The reason for this is probably that protonated pyrrole shows increased hydrophilicity and hence lower affinity for CNT surfaces. The lower the pH, the higher the degree of protonation of pyrrole and the greater the degree of dissociation of pyrrole molecules from the CNT surface. Below pH 0, almost all of the pyrrole molecules are protonated, and hence nanocables can not be obtained.

The standard Van Der Pauwe dc four-probe method[23] was used to measure the electron transport behavior of polypyrrole and nanocables (Figure 5). Polypyrrole synthesized in the presence of CTAB showed typical nonmetallic behavior[24] with a room-temperature conductivity of 7.3×10^{-3} S cm^{-1} (the room-temperature conductivity of CNTs is 0.23 S cm$^{-1[25]}$). The low room-temperature conductivity of polypyrrole is probably due to its low degree of doping. The overall pattern of temperature-dependent conductivity of polypyrrole is well described by Mott's law for quasi-one-dimensional, variable-range hopping.[26] In contrast, the electron-transport properties of CTAB-directed polypyrrole/CNT nanocables exhibit the following remarkable characteristics: 1) Low- and room-temperature conductivities both increase with increasing fraction of CNT; 2) the maximum room-temperature conductivity of nanocables (0.231 S cm^{-1}) is one order of magnitude higher than that of polypyrrole; 3) the low-temperature conductivity is much higher than that of polypyrrole; 4) the temperature dependence of the conductivity is much weaker than that of polypyrrole, probably because the conductivities at different temperatures were dominated by different components;[11] 5) nevertheless, the conductivity is still well described by Mott's law for variable-range hopping. Taken together, these facts indicate
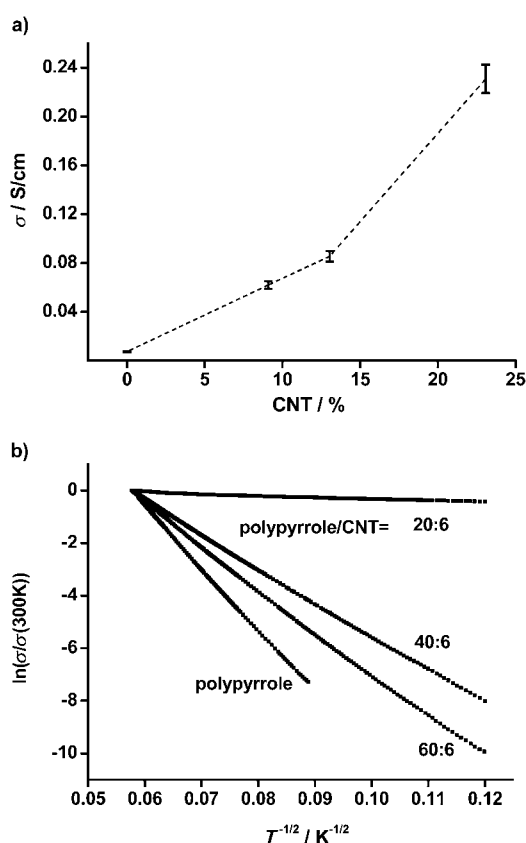

Figure 5. a) Room-temperature conductivities of nanocables with fractions of CNT varying from 0 to 25%; b) normalized temperature dependence of conductivity for nanocables with different polypyrrole/CNT mass ratios.

that electrical contacts between polypyrrole and CNT have been improved and that the cablelike structure favors charge transfer between polypyrrole and CNT. Furthermore, in comparison with CTAB, Oπ-10 is superior in directing the synthesis of nanocables with high electron transport properties. For example, at a CNT content of 9.1%, the room-temperature conductivity of the nanocables directed by Oπ-10 is 0.215 S cm^{-1}, whereas that of nanocables directed by CTAB was only 0.062 S cm^{-1}. This is probably attributable to partial avoidance of overoxidation and the more ordered arrangement of polypyrrole chains in the presence of Oπ-10.[27]

Magnetoresistance (MR) is sensitive to the extent of structural disorder and therefore serves as an especially useful probe for identifying microscopic transport mechanisms *and* scattering processes.[28] Nanocables with a polypyrrole/CNT mass ratio of 10/3 show negative MR at 3–100 K (Figure 6). The data indicate that electrons transferred within the nanocable form a conventional diffusive system, describable within the framework of weak-localization theory. In this case the effect of e–e interaction can be treated as a perturbation.[29] Carbon nanotubes synthesized by CVD also show negative MR at low temperature.[29]

In summary, we have described a simple approach to the synthesis of size-controllable polypyrrole/CNT nanocables. Different types of surfactants were applied to overcome the difficulty of dispersing CNT into an insoluble and infusible polymer
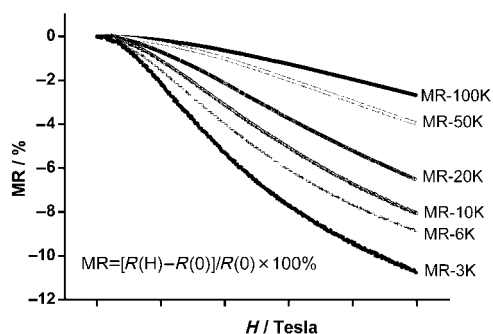
Figure 6. *Magnetoresistance of nanocables (pyrrole/CNT mass ratio 20/6) as a function of magnetic field at different temperatures.*

matrix, and pyrrole was polymerized in situ at the surface of the CNTs (core layer) to ultimately form the outer shell of the nanocables. By changing the pyrrole/CNT ratio, we can easily control the size of as-prepared nanocables. Polypyrrole/CNT nanocables produced in this way show enhanced electrical properties; a negative temperature coefficient of resistance at 77–300 K and negative magnetoresistance at 10–200 K were observed. These characteristics of size-controllability and enhanced electrical properties provide new potential for applications for nanocables in a number of scientific and technological fields.

Experimental Section

Pyrrole monomer (98%, Aldrich Chemical Co.) was distilled under reduced pressure. CNTs were synthesized by ethylene CVD with Al_2O_3-supported Fe catalysts, as described in a previous study.[12] Other reagents, including CTAB, APS (both analytically pure, from Beijing Chemical Co. of China) and Oπ-10 (chemically pure, from Beijing Chemical Co. of China), were used without further purification.

Polypyrrole/CNT nanocables were synthesized by in situ chemical oxidative polymerization directed by surfactants. In a typical synthesis, CTAB (0.124 g) or Oπ–10 (1.5 g) and CNTs (6 mg) were added to deionized water (31 mL), sonicated for over 2 h to obtain well-dispersed suspensions, then cooled to 0–5 °C. A precooled solution of pyrrole monomer (0.06 mL) and a solution of deionized water (6.25 mL) containing ammonium persulfate (0.204 g) were added sequentially to the suspension. The reaction mixture was sonicated for 2 min then allowed to stand at 0–5 °C for 24 h. The resulting black precipitate was collected by filtration and rinsed several times with distilled water and methanol. The filter cake was then dried under vacuum at room temperature for 24 h.

Infrared spectra were recorded with a Magna-IR 750 system on powder samples. SEM was conducted at 10 kV with a XL30S-FEG field-emission instrument, and HRTEM images were recorded on a Tecnai F30 at 300 kV. Samples for SEM and TEM were prepared by placing a drop of as-made aqueous dispersion of nanocables onto a silicon wafer and carbon-coated copper grid, respectively. Electrical conductivity was measured with a Keithley 220 programmable current source and 181 nanovoltmeter, which was autocontrolled by a computer. Magnetoresistance was measured with a PPMS (physical properties measurement system from Quantum Design, USA). The applied magnetic field was perpendicular to the surface

of the sample. Samples used in dc electrical-conductivity and magnetoresistance measurements were pressed pellets (12 mm in diameter and about 0.1 mm in thickness), obtained by applying a hydraulic pressure of about 10 MPa.

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